THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES

NUMBER 85

THE REACTION OF TALL OIL FATTY ACIDS DURING SIMULATED OXYGEN-ALKALI DELIGNIFICATION. 1. EFFECTS OF REACTION VARIABLES

GERALD R. MITTET AND NORMAN S. THOMPSON

MAY, 1979

The reaction of tall oil fatty acids during simulated oxygen delignification

1. Effects of reaction variables

Gerald R. Mittet and Norman S. Thompson
The Institute of Paper Chemistry, Appleton, Wis. 54912

Keywords: tall oil; fatty acids; chemical degradation; delignification; oxygen; alkalis; oxygen pulping; process variables

ABSTRACT

The reactions of tall oil fatty acids and esters were investigated under conditions simulating those of oxygen-alkali delignification. A 2^5 half factorial experimental design covered the effects of temperature, reaction time, oxygen pressure, alkali, and substrate on the degradation of methyl oleate and methyl linoleate. Alkali had the most pronounced effect of these variables. In contrast to the behavior of carbohydrates and lignin, fatty acids and esters were relatively stable in oxygen-hydroxide, and were extensively oxidized in oxygen-bicarbonate. Those fatty acid esters which were not degraded by the oxygen and bicarbonate were not saponified and were not converted to water-soluble soaps. These results suggest that tall oil fatty acid recovery from oxygen-bicarbonate or oxygen-carbonate delignification will not be possible without some type of pretreatment. In reaction systems containing bicarbonate, wood exerted an apparent inhibition with regard to fatty acid autoxidation. More extensive degradation of the fatty acid esters occurred when wood meal was replaced with cotton linters. The protective effect of wood was lost or diminished by sodium hydroxide.

This paper has been submitted for publication in Tappi.

Introduction

Although oxygen-alkali pulping has been investigated as an alternative to kraft pulping, tall oil recovery has not been considered in that research. Tall oil is a valuable by-product which, if lost, would offset some of the benefits of oxygen-alkali pulping. The reactions of tall oil components during oxygen-alkali deliginification were discussed by Hrutfiord and Hopley (1) who compared soda with soda-oxygen pulping and found that inclusion of oxygen markedly reduced tall oil yield. Erickson and Dence (2), delignifying thermomechanical pulp with oxygen and hydroxide observed similar results. Pearl and Dickey (3) reported that some of the tall oil loss incurred during oxygen-alkali delignification of wood chips could be attributed to retention of fatty and resin acids in the washed pulp. The present investigation was undertaken to systematically examine and compare the effects of selected parameters on the reactions of tall oil fatty acids with oxygen and alkali under conditions simulating those of oxygen-alkali delignification.

Five reaction variables studied were reaction temperature, reaction time, oxygen pressure, alkali, and substrate. Arbitrarily chosen high and low levels, representing the probable extremes of an oxygen-alkali delignification process, were assigned to each variable. Those assignments, which are listed in Table I, were made on the assumption that changing any variable from its low level to its high level would increase fatty acid degradation. Only the reactions of fatty acids, which constitute one of the important fractions of crude tall oil, were examined.

[Table I here]

Besides time, temperature and oxygen pressure, alkali was included to determine if a bicarbonate- or hydroxide-based delignification system would be more conducive to recovery of the tall oil fatty acids. The substrate was varied to see if lignin would inhibit fatty acid oxidation. Since more extensive oxidation was expected when the lignin content was low, cotton linters was defined as the higher level of the substrate variable. Prior to each reaction, the substrate, either cotton or wood meal, was impregnated with a mixture of methyl oleate and methyl linoleate. We investigated the reactions of only these two compounds because oleic acid and linoleic acid are by far the two most important tall oil fatty acids (4).

[Chemical structure here]

Although fatty acids occur in wood primarily as triglyceride esters, we used methyl esters because we could readily procure and analyze them.

Because of the number of variables considered in the experimental program, we used a 2^5 half factorial experimental design (5). Sixteen different reactions were required to satisfy the design; each variable was assigned to its high level in exactly eight of them, and to its low level in the remaining eight. The complete half factorial experimental design is outlined in Table II.

[Table II here]

For any designated response, the half factorial design permits determination of five main effects, one for each variable, and the ten two-factor interactions between variables. A main effect is defined as the overall change in the response, averaged over all reactions, which occurs when a variable is raised from its lower level to its higher level.

The main effect of any specific variable is determined by calculating the average response of all those reactions which involve the variable only at its lower level, and subtracting that quantity from the average response of those reactions involving the variable only at its higher level. A two-factor interaction exists if the effect of one variable is dependent upon the level of another.

Three-factor interactions exist if the two-factor interaction between any two variables is dependent upon the level of a third variable. Similarly, a four-factor interaction exists when a three-factor interaction is dependent upon the level of a fourth variable. In a full factorial experimental design, all main effects and interactions may be determined unequivocally. However, the magnitudes of the higher order interactions are often negligibly small in comparison with the magnitudes of the main effects and two-factor interactions. In the half factorial design developed for this investigation, the four-factor interaction involving any four variables is equated with the main effect of the fifth variable. The three-factor interaction among any three variables is equated with the two-factor interaction between the other two. To determine the main effects and two-factor interactions, all three- and four-factor interactions are presumed to be zero.

To calculate main effects and interactions, suitable responses must be defined and measured for each reaction. In the present case, two responses, the total percent yields of unoxidized oleate and linoleate, were measured in each reaction. The total yields corresponded to the combined yields of methyl esters and free fatty acids measured for each component after each reaction. Two main effects, one for each response,

were determined independently for each variable. Similarly, two separate two-factor interactions were calculated for each pair of variables.

Experimental

Wood meal was prepared by grinding loblolly pinewood chips in a Wiley mill to pass through a plate perforated with 1/8 inch diameter holes. The wood meal was extracted thoroughly with acetone to remove all naturally occurring tall oil components, washed successively with SO_2 water and distilled water to decrease its metal ion content, and then air dried. All oxidations were carried out in a 1-L stainless steel reaction vessel. Prior to each reaction, the fatty acid methyl esters (1.72 g methyl oleate and 2.12 g methyl linoleate) were dissolved in acetone and slurried with the substrate, which consisted of either wood meal (50 g) or cotton linters (30 g). Less cotton than wood was employed because of its greater water absorption. The acetone was then driven off by evaporation under reduced pressure, leaving the substrate impregnated with the fatty acid esters. The reaction vessel, containing 175 mL of distilled water, was preheated on a boiling water bath to 80°C. The alkali, either sodium hydroxide (11 g) or sodium bicarbonate (23.1 g), was then dissolved in the water, and that solution was mixed thoroughly with the ester-impregnated substrate, leaving a porous plug of alkali, water, substrate, and fatty acid esters. The reactor was then sealed, purged with oxygen, and pressurized to the nominal reaction pressure with oxygen. The charged reactor was immediately lowered into an oil bath which had been preheated to the predetermined reaction temperature, and measurement of the reaction time commenced. At the end of each reaction, the vessel was cooled in ice water and vented to atmospheric pressure. The alkaline reaction

product was acidified with sulfuric acid and filtered on a coarse sintered glass funnel. The filtrate and the residual substrate were both extracted with ether for twenty-four hours in continuous extractors. The ether extracts were combined and fractionated into neutrals and weak acids as described by Zinkel and Rowe (6). The neutrals, which contained unsaponified fatty acid methyl esters, and the weak acids, containing free fatty acids, were analyzed by gas liquid chromatography on a 6-ft stainless steel column packed with 10% EGSS-X on 100/120 Gas Chrom P at a temperature of 170°C. The free fatty acids were first converted to methyl esters with diazomethane, and methyl eicosanoate internal standard was added to both fractions. The carrier gas was helium at a flow rate of 25 mL/min, and the gas chromatograph was equipped with a flame ionization detector.

Results and discussion

Results of the half factorial experimental design are presented in Tables III, IV and V. Listed in the first of those tables are the yields of unoxidized fatty acid methyl esters, free fatty acids, and their total combined yields. We used total yields for calculating main effects and interactions. In general, methyl linoleate was degraded considerably more than methyl oleate, as was expected (7). The first step of fatty acid autoxidation (oxidation by molecular oxygen) is abstraction of a hydrogen atom and formation of a free radical. In unsaturated compounds, allylic hydrogen atoms bonded to carbon atoms adjacent to the double bonds are abstracted preferentially. Methyl oleate contains two reactive sites, located on either side of the double bond, while methyl linoleate contains a particularly reactive "activated" methylene group between the two double bonds. Because of the ease with which a hydrogen atom is

abstracted from that methylene unit, methyl linoleate undergoes autoxidation more rapidly than methyl oleate.

[Tables III, IV and V here]

The main effects of all variables, and all of their two-factor interactions, are presented in Tables IV and V. Listed in Table IV are the main effects and interactions related only to the total yield of oleate, while the effects and interactions shown in Table V relate only to the total yield of linoleate. Included in each table is an analysis of variance to determine which effects and interactions may be considered significant. The significance of each main effect and interaction is tested by comparing its mean square with an error mean square term derived from the results of reactions 17-21. If the probability that an observed main effect of interaction results from experimental error is less than 1%, then the effect or interaction is considered highly significant, as indicated by a double asterisk (**). If that probability is greater than 1% and less than 5%, then the effect of interaction is considered significant and is so designated by a single asterisk (*). Other effects or interactions are considered possibly significant, with less than a 10% error probability, if their F-tests exceed 5.54.

Almost all of the main effects are significant or highly significant. The main effect of temperature related to the yield of linoleate is probably significant, although its F-test falls slightly below the 5% level. Although the main effect of substrate related to the yield of oleate is not itself significant, the substrate did interact significantly with both pressure and alkali. All of the main effects possess negative signs, which

shows that raising any variable from its low level to its high level decreases the yields of oleate and linoleate. Alkali is the most influential variable. Substituting sodium bicarbonate for sodium hydroxide decreased the average yields of oleate and linoleate by more than 30%.

The main effect of substrate is also negative, indicating that fatty acid yields decrease if cotton is substituted for wood. Substrate is, however, involved in two significant interactions. The pressure-substrate interaction has a positive sign, showing that the effect of pressure is more pronounced at the lower level of substrate and that the effect of substrate is greater at the lower level of pressure. In the presence of wood meal, higher oxygen pressure causes substantial decreases in fatty acid yields. Conversely, wood exhibits a "protective effect" toward fatty acid autoxidation at high pressure. On the other hand, oxygen pressure does not influence fatty acid oxidation in the presence of cotton.

The alkali-substrate interaction has a negative sign and a relatively large magnitude. The effect of alkali is greater in the presence of cotton, therefore, than in the presence of wood. However, in either system, replacing hydroxide with bicarbonate results in decreased yields of both oleate and linoleate. On the other hand, while wood meal inhibits fatty acid oxidation in the presence of bicarbonate, the substrate effect is reversed in the presence of hydroxide. When hydroxide is used, substituting cotton for wood meal results in an average increase in the yields of oleate and linoleate, which is the opposite of what is found with bicarbonate.

The inhibitory effect of wood on fatty acid oxidation may result from oxygen diffusivity limitations, as indicated by the pressure-substrate interaction, or it may derive from the antioxidant characteristics of lignin-derived phenols. Phenolic antioxidants are used to effectively retard the autoxidation of fats and oils (8), and the presence of phenols in oxygen-alkali spent liquor has been demonstrated (9). Those phenols might lose their antioxidant properties when ionized, which could account in part for the alkali-substrate interaction. The phenols exist in their unionized states in the presence of bicarbonate and are ionized by hydroxide. On the other hand, the alkali-substrate interaction may reflect the rapid and extensive pH drop which occurs when wood reacts with oxygen and sodium hydroxide. As indicated by the high magnitude of the alkali main effect, the fatty acids should be autoxidized more rapidly as the pH drops. A less dramatic pH drop is expected in the cotton-hydroxide system. Therefore, the high magnitude of the alkali effect in the presence of cotton alone suggests a very large pH differential between the bicarbonate- and hydroxide-based reactions. That pH differential is diminished in the presence of wood, and the alkali effect subsequently decreases. The beneficial effect of wood in systems containing hydroxide might be overwhelmed by an effect resulting from the decrease in pH which occurs as the hydroxide is consumed.

The effect of alkali on the oxidation of fatty acids contrasts with its effect on the autoxidation of carbohydrates and lignin. Degradation of the latter substances is promoted by hydroxide, while degradation of the fatty acids is promoted by bicarbonate. However, as examination of the results in Table III will show, the fatty acid esters were saponified by the hydroxide and not by the bicarbonate. To insure that the alkali

effect did not reflect differences in the reactivity between fatty acid methyl esters and fatty acid soaps, two additional oxidations of free fatty acids were conducted under differing alkali conditions. The reaction conditions and yields of unoxidized starting material are shown in Table VI.

[Table VI here]

Consistent with the results observed during the oxidations of fatty acid methyl esters, the free fatty acids underwent much more extensive degradation in the presence of sodium bicarbonate. The enhanced reactivity of the fatty acids and their derivatives in the presence of bicarbonate may in part be due to the formation of carbonate radicals created during reactions between hydroxyl radicals and carbonate or bicarbonate ions (10). In systems containing large quantities of bicarbonate or carbonate, relatively high steady state concentrations of those radicals might be attained, and they might initiate fatty acid autoxidation. The hydroxyl radicals themselves can initiate fatty acid oxidation, and those highly reactive radicals could interact directly with the substrate to a greater extent than the carbonate radicals. The participation of carbonate radicals in the oxidation reactions is only speculated, since not enough information is available to understand the alkali effect.

Conclusions

1. Although unsaturated tall oil fatty acids and their esters autoxidize during oxygen-alkali delignification, degradation of the acids is not complete except under very severe reaction conditions. Tall oil fatty acid recovery may be compatible with oxygen-alkali delignification.

2. Alkali is the most critical variable affecting reactions of the tall oil fatty acids. The fatty acids and their esters were much more extensively degraded in the presence of bicarbonate than they were with hydroxide under otherwise identical reaction conditions. This behavior, which is the opposite of that observed for carbohydrates or lignin, may result from the accumulation of carbonate radicals in the reaction system. Furthermore, those fatty acid esters which did survive treatment with oxygen and bicarbonate were not saponified, and they could not be washed from pulp with water. Recovery of tall oil fatty acids will probably be eliminated in an oxygen-alkali delignification process which utilizes bicarbonate or carbonate exclusively.

3. When bicarbonate was used, the fatty acid esters were more stable in the presence of wood meal than in the presence of cotton linters. This stability did not occur when sodium hydroxide was used.

Literature cited

1. Hrutfiord, B. F., and Hopley, S. M., International Symposium on Delignification with Oxygen, Ozone and Peroxides. Raleigh, North Carolina, May, 1975.

2. Erickson, M., and Dence, C. W., Tappi 58(8): 190 (1975).

3. Pearl, I. A., and Dickey, E. E., Tappi 60(10): 126 (1977).

4. Zinkel, D. F., Tappi 58(2): 118 (1975).

5. Davies, O. L., ed., "The Design and Analysis of Industrial Experiments," New York, Hafner Publishing Company, 1963. 636 p.

6. Zinkel, D. F., and Rowe, J. W., Anal. Chem. 36: 1160 (1964).

7. Holman, R. T., "Autoxidation of Fats and Related Substances." In Progress in the Chemistry of Fats and Other Lipids. Vol. 2. p. 51, New York, Academic Press, 1954.

8. Ingold, K. U., Chem. Rev. 61: 563 (1961).

9. Scholander, E., Durst, W. B., Pearce, G., and Dence, C. W., Tappi 57(3): 142 (1974).

10. Behar, D., Czapski, G., and Duchovny, I., J. Phys. Chem. 74: 2206 (1970).

I. Reaction variables

Variable	Low level	High level
Temperature, °C	100	160
Reaction, time, hr	2	8
Oxygen pressure[a], kPa	690	3500
Alkali[b]	11 g NaOH	23.1 g $NaHCO_3$
Substrate[c]	50 g wood meal	30 g cotton linters

[a]6.9 kiloPascals = 1.0 psi. [b]The alkali charge in all reactions was 17%, as Na_2O, based on o.d. wood. [c]All reactions were conducted at high consistency.

II. Half factorial design for oxidations of fatty acid methyl esters

Reaction no.	Temp., °C	Reaction time, hr	O_2 Pressure, kPa	Alkali	Substrate
1	100	2	690	NaOH	Cotton
2	160	2	690	NaOH	Wood
3	100	8	690	NaOH	Wood
4	160	8	690	NaOH	Cotton
5	100	2	3500	NaOH	Wood
6	160	2	3500	NaOH	Cotton
7	100	8	3500	NaOH	Cotton
8	160	8	3500	NaOH	Wood
9	100	2	690	$NaHCO_3$	Wood
10	160	2	690	$NaHCO_3$	Cotton
11	100	8	690	$NaHCO_3$	Cotton
12	160	8	690	$NaHCO_3$	Wood
13	100	2	3500	$NaHCO_3$	Cotton
14	160	2	3500	$NaHCO_3$	Wood
15	100	8	3500	$NaHCO_3$	Wood
16	160	8	3500	$NaHCO_3$	Cotton
17[a]	130	5	2100	NaOH	Wood
18[a]	130	5	2100	NaOH	Wood
19[a]	130	5	2100	NaOH	Wood
20[a]	130	5	2100	$NaHCO_3$	Wood
21[a]	130	5	2100	$NaHCO_3$	Wood

[a]Reactions 17-21 were not part of the actual half factorial design and were included for estimation of experimental error.

III. Yields of unoxidized oleate and linoleate

Reaction no.	Yield of starting material[a] (g, as methyl esters)						Total yield, %	
	Methyl esters		Free fatty acids		Total			
	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate
1	0.01	0.01	1.49	1.58	1.50	1.59	87.2	75.0
2	0.10	0.05	1.28	1.31	1.38	1.36	80.2	64.2
3	0.08	0.06	1.30	1.43	1.38	1.49	80.2	70.3
4	0	0	1.39	1.05	1.39	1.05	80.8	49.5
5	0.28	0.22	0.94	1.05	1.22	1.27	70.9	59.9
6	0	0	1.27	0.98	1.27	0.98	73.8	46.2
7	0	0	1.39	1.38	1.39	1.38	80.8	65.6
8	0.08	0.02	0.46	0.30	0.54	0.32	31.4	15.1
9	1.37	1.31	0.02	0.02	1.39	1.33	80.8	62.7
10	0.36	0.28	0.02	0.01	0.38	0.29	22.1	13.7
11	0.39	0.02	0.02	0.01	0.41	0.03	23.8	1.4
12	0.77	0.73	0.09	0.10	0.86	0.83	50.0	39.2
13	1.03	0.20	0.02	0	1.05	0.20	61.0	9.4
14	0.53	0.84	0.02	0.02	0.55	0.86	32.0	40.6
15	0.77	0.49	0.02	0.01	0.79	0.50	45.9	23.6
16	0.16	0.08	0.02	0.02	0.18	0.10	10.5	4.7
17[b]	0.33	0.16	0.60	0.58	0.93	0.74	54.1	34.9
18[b]	0.12	0.05	1.06	1.06	1.18	1.11	68.6	52.4
19[b]	0.29	0.12	0.84	0.93	1.13	1.05	65.7	49.5
20[b]	0.69	0.64	0.01	0.01	0.70	0.65	40.7	30.7
21[b]	0.78	0.70	0.01	0.01	0.79	0.71	45.9	33.5

[a]All reaction systems initially contained 1.72 g methyl oleate and 2.12 g methyl linoleate. [b]Reactions 17-21 were not part of the half factorial experimental design (reactions 1-16), but were included for estimation of error.

IV. Main effects and two-factor interactions related to the total yield of oleate

Main effect	Degrees of freedom	Sum of squares	Mean square	F-Test (mean sq/EMS)	Sign and magnitude of effect or interaction
Temperature	1	1402.5	1402.5	32.09*	-18.7*
Reaction time	1	683.8	683.8	15.65*	-13.1*
Oxygen pressure	1	610.1	610.1	13.96*	-12.4*
Alkali	1	4199.0	4199.0	96.09**	-32.4**
Substrate	1	61.6	61.6	1.41	-3.9
Interaction					
Temperature-time	1	71.4	71.4	1.63	+4.2
Temperature-pressure	1	324.0	324.0	7.41	-9.0
Temperature-alkali	1	121.0	121.0	2.77	-5.5
Temperature-substrate	1	21.6	21.6	0.49	+2.3
Time-pressure	1	70.6	70.6	1.62	-4.2
Time-alkali	1	44.9	44.9	1.03	-3.4
Time-substrate	1	4.2	4.2	0.10	+1.0
Pressure-alkali	1	122.1	122.1	2.79	+5.5
Pressure-substrate	1	948.6	948.6	21.71*	+15.4*
Alkali-substrate	1	1428.8	1428.8	32.70*	-18.9*
Error estimate					
Reactions 17-19	2	117.7	(Sums of squares about the means)		
Reactions 20-21	1	13.5			
Reactions 17-21	3	131.2	43.7 = Error mean square (EMS)		

[a]The significance levels of the F-test are 5.54 at the 10% level, 10.1 at the 5% level and 34.1 at the 1% level. An effect or interaction is considered highly significant (**) if its mean square exceeds 1490.2, significant (*) if its mean square is between 441.4 and 1490.2, and possibly significant if its mean square is below 441.4 but greater than 242.1.

V. Main effects and two-factor interactions related to the total yield of linoleate

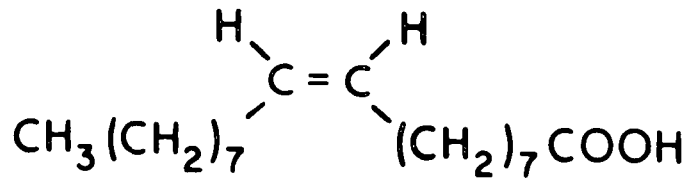
Main effect	Degrees of freedom	Sum of squares	Mean square	F-Test (mean sq/EMS)	Sign and magnitude of effect or interaction
Temperature	1	560.5	560.5	9.42	-11.8
Reaction time	1	654.1	654.1	10.99*	-12.8*
Oxygen pressure	1	768.7	768.7	12.92*	-13.9*
Alkali	1	3921.9	3921.9	65.91**	-31.3**
Substrate	1	757.6	757.6	12.73*	-13.8*
Interaction					
Temperature-time	1	6.4	6.4	0.11	-1.3
Temperature-pressure	1	5.2	5.2	0.09	-1.1
Temperature-alkali	1	586.9	586.9	9.86	+12.1
Temperature-substrate	1	25.3	25.3	0.43	+2.5
Time-pressure	1	4.1	4.1	0.07	+1.0
Time-alkali	1	10.1	10.1	0.17	-1.6
Time-substrate	1	196.7	196.7	3.31	+7.0
Pressure-alkali	1	70.1	70.1	1.18	+4.2
Pressure-substrate	1	435.8	435.8	7.32	+10.4
Alkali-substrate	1	1674.9	1674.9	28.15*	-20.5*
Error estimate					
Reactions 17-19	2	175.9	(Sums of squares about the means)		
Reactions 20-21	1	3.9			
Reactions 17-21	3	179.8	59.5 = Error mean square (EMS)		

[a]The significance levels of the F-test are 5.54 at the 10% level, 10.1 at the 5% level and 34.1 at the 1% level. An effect or interaction is considered highly significant (**) if its mean square exceeds 2029.0, significant (*) if its mean square is between 601.0 and 2029.0, and possibly significant if its mean square is below 601.0 but greater than 329.6.

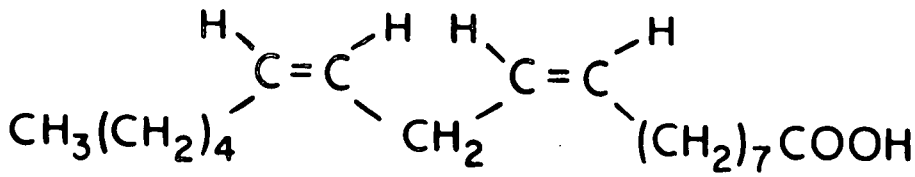
VI. Oxidations of free fatty acids[a]

Reaction no.	Alkali	Substrate	Weights of fatty acids, g				Yields of fatty acids, %	
			Starting material		Reaction product			
			Oleic	Linoleic	Oleic	Linoleic	Oleic	Linoleic
22	NaOH	Cotton	1.54	2.23	1.34	1.47	87.0	65.9
23	$NaHCO_3$	Cotton	1.54	2.23	0.19	0.01	12.3	0.4

[a]Both reactions were conducted at 130°C for 5 hours under an initial oxygen pressure of 2100 kPa.



oleic acid



linoleic acid